Emissions reductions have also been found when tire derived fuel was burned in a precalciner. In one case, when 47 percent of the coal fired in the calciner was substituted with tire-derived-fuel, a reduction in NO_x emissions of about 29 percent was observed.[35]

4.2.7 Mid-Kiln Firing

The concept of staged combustion of fuels may also be used in conventional wet and long-dry kilns by injecting solid fuel into the calcining zone of a rotating long kiln using a specially designed feed injection mechanism.[36] This system is known as mid-kiln firing (MKF) and allows part of the fuel to be burned at a material calcination temperature of 600 to 900°C (1100 to 1650°F) which is much lower than the clinker burning temperature of 1200 to 1480°C (2200 to 2700°F).[28]

To maintain a continuity in the heat input, solid and slow burning fuels (such as tires) are most amenable for MKF. The Cadence feed fork MKF technology was first introduced in 1989. It can be installed during an annual maintenance shutdown. It is comprised of three primary components: (1) a staging arm or 'feed fork' that picks up the fuel modules and positions them for entry into the kiln, (2) two pivoting doors that open to allow the fuel modules to drop into the kiln, and (3) a drop tube that extends through the side wall of the kiln. In addition to these basic components, feed fork technology also requires a delivery system which positions the fuel models so they can be picked up by the feed fork and a mechanism for opening the doors so the fuel modules can enter the kiln.[37] Due to the rotation of the kiln, fuel can be conveniently injected only once per revolution from the top.

Although most feed forks today are dedicated to whole tires, one facility uses baled industrial waste as a fuel, and many others are investigating a variety of energy containing waste materials from carpet scrap to pharmaceutical waste. These energy-bearing waste materials can be containerized or dementionalized into discrete fuel modules to be fed to the kiln using the feed fork.[37]

Inserting whole tires into mid-kiln locations can give precalciner stability to the kiln. The operators have two points of control to assist in stabilizing kiln operation. Tires burn for 15 to 20 minutes within the kiln after entry. This is deduced from observations of the rate of change in kiln exit oxygen levels after entry of tires begins. With proper instrumentation, control of the kiln can be improved by adding solid fuels midkiln.[39]

Mid-kiln firing of tires or other waste-derived fuels does not reduce the final product quality; in fact, many of Cadence's cement kiln partners have reported an improvement in the clinker burnability and mineralogy. The enhanced control has shown to impart better formation of clinker. Reductions in cement fineness have been shown while maintaining similar seven-day strengths. Several facilities also have reported an extended life of the refractory in the burn zone.[37,39]

By adding fuel in the main flame at mid-kiln, MKF changes both the flame temperature and flame length. These changes may reduce thermal NO_x formation by burning part of the fuel at a lower temperature and by creating reducing conditions at the solid waste injection point which may destroy some of the NO_x formed upstream in the kiln burning zone. MKF may also produce additional fuel NO_x depending upon the nitrogen content of the fuel.[38] However, as discussed in section 5.1.3, fuel NO_x is unimportant relative to thermal NO_x formation. Additionally the discontinuous fuel feed from MFK can result in increased CO emissions especially if hazardous wastes are used. To control CO emissions, the kiln may have to have increased combustion air which can decrease production capacity.[40]

According to literature from Cadence, in tests of its feed fork technology, one kiln reduced NO_x emissions by 38%, overall particulate emissions by 14%, metal emissions by 30%, SO_2 emissions by 36%, and net emissions of all hydrocarbons by 29%.[37,39] In the research conducted for this report, test data were compiled for seven dry kilns and three wet kilns with MKF technology. In nine tests on the dry kilns, the average reduction in NO_x emissions was 33%, with a range from 11% to 55%. In three tests on the wet kilns, the average reduction in NO_x emissions 40%, with a range from 28% to 59% (see Table 4-8).[40,41,42,43,44] It should be noted that the three kilns that are known to have CEMS all reported emissions reductions of 45 percent or more.

Table 4-4.6. Emissions From Kilns With Mid-Kiln Firing

	Emissions (lb NOx/ton of clinker)	Percent Reduction (%)	Emissions Based on CEMS Data
Dry Kilns[a]			
A[40]	not given	13.6	unknown
B[40]	not given	11.1	unknown
C[24,44]	not given	45.1	yes
C[40]	not given	55.3	yes
D[21,41]	2.7	not given	unknown
E[22,42]	10.2	13.9	unknown
F[40]	not given	46.6	unknown

	Emissions (lb NOx/ton of clinker)	Percent Reduction (%)	Emissions Based on CEMS Data
F[40]	not given	50.4	unknown
F[40]	not given	28.3	unknown
Average (Dry Kilns)	6.4	33.3	
Wet Kilns			
G[23,43]	not given	59.0	yes
H[40]	not given	35.0	unknown
I[40]	not given	27.6	unknown
Average (Wet Kilns)	n/a	40.5	
Average (Dry & Wet Kilns)	6.4	35.1	

[a] There was more than one test at some kilns.

Waste-derived fuels with high heating values represent an economical source of energy for the cement industry and its consumption has been increasing during the past decade.[12] Midkiln firing is a proven technology and so far at least 21 long kilns in the U.S. and nearly 40 kilns worldwide have been modified to allow mid-kiln firing of solid and hazardous waste.[37, 15]

4.3   Lower Temperature Oxidation Based Technologies

Oxidation technologies were not evaluated in the EPA 2000 Report. One of these technologies, LoTOx, is currently being installed in refineries at fluidized catalytic cracking units (FCCUs). The temperatures, gas flow rates and other characteristics of FCCUs are similar enough to cement plants that these technologies should be considered as candidates for evaluation as transferable technologies to application at cement kilns.

4.3.1   Introduction

Oxidation technologies for flue gas NO_x control developed in recent years have become commercially successful and economically viable as an alternative to ammonia and urea based technologies using reduction chemistry to remove NO_x. Commercially available technologies such as Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR), which reduce NO_x to nitrogen using ammonia or urea as an active chemical are optimized to specific temperature windows and have similar reagent costs for the varying ammonia based reagents. Oxidation technologies can work in other temperature regimes and use different reagents that are not linked to ammonia costs and, thereby, provide important control options to ammonia-based NO_x reduction technologies.

Oxidation technologies convert lower nitrogen oxides such as nitric oxide (NO) and nitrogen dioxide (NO_2) to higher nitrogen oxides such as nitrogen sesquioxide (N_2O_3) and nitrogen pentoxide (N_2O_5). These higher nitrogen oxides are highly water soluble and are efficiently scrubbed out with water as nitric and nitrous acids or with caustic solution as nitrite or nitrate salts. NO_x removal in excess of 90% has been achieved using oxidation technology on NO_x sources with high sulfur content, acid gases, high particulates and processes with highly variable load conditions. Generally these technologies work at relatively low temperatures (100-950 °F) and some of these technologies are likely most cost effective for use on plants with existing scrubbers. But may also prove to be cost effective options due to their potential application in lower temperature windows which can avoid expensive options like gas reheat. These technologies are used for NO_x control for a variety of NO_x emission sources but are not known to have been used to date on a cement kiln.

4.3.2 LoTOx

General description. The LoTOx^{TM} System uses ozone as the oxidizing agent, which selectively oxidizes relatively insoluble NO_x to higher oxides of nitrogen. These higher oxides are readily soluble and easily removed in a wet scrubber. The patented system, which can be installed as a stand-alone or retrofit design, provides sufficient residence time under maximum load conditions to allow complete reaction of the ozone. The system's small and adaptable footprint, as well as its ability to produce ozone on demand, provides control of the installation to maximize NO_x control and minimize capital and operating costs. The LoTOx^{TM} System is very selective for NO_x removal, oxidizing only the NO_x and therefore efficiently using the treatment chemical, ozone, without causing any significant SOx oxidation and without affecting the performance of the downstream SOx scrubber.

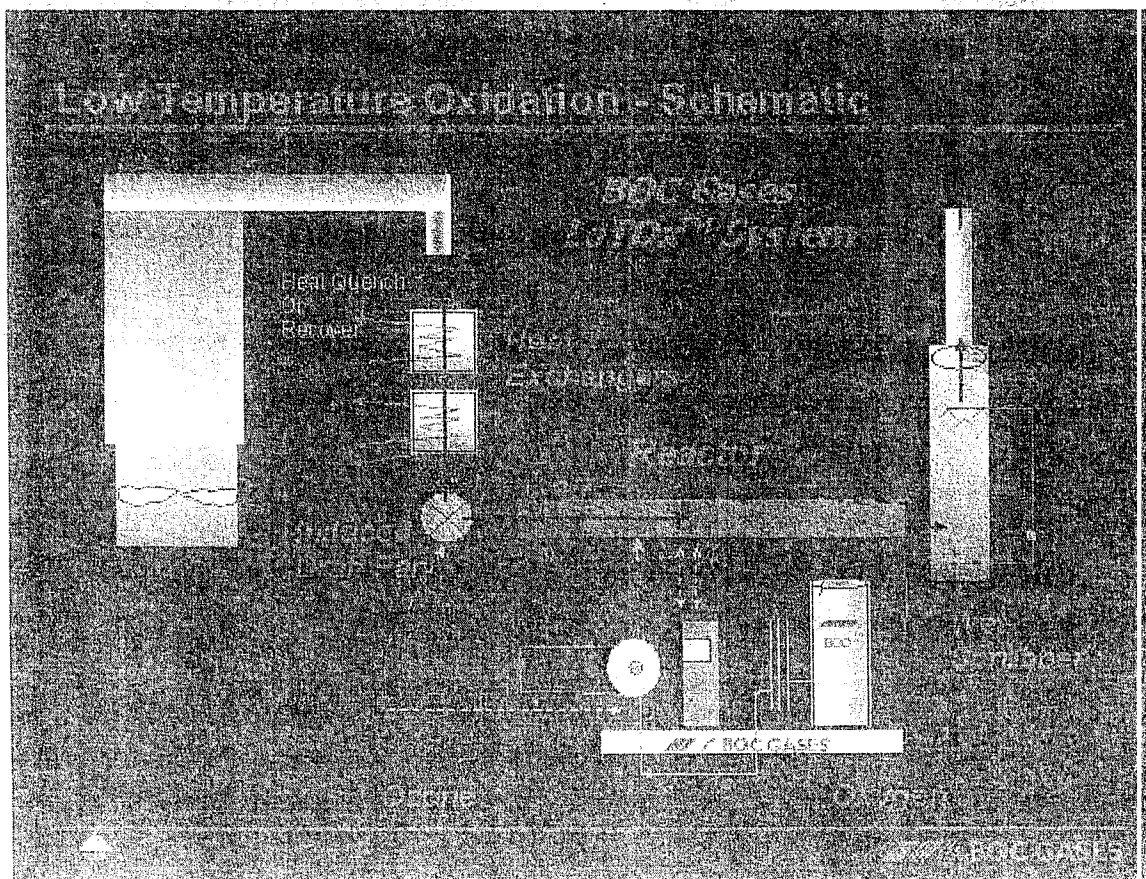Figure 4-3.1. is an overall process diagram of the LoTOx^{TM} System.

Figure 4-3.1. Overall Process Diagram of the LoTOx^{TM} System

Figure 4-3.2. provides another example of a LoTOx^{TM} system where the ozone injection is included in the scrubber.

EDV® Wet Scrubbing System With LoTOx^{TM} injection
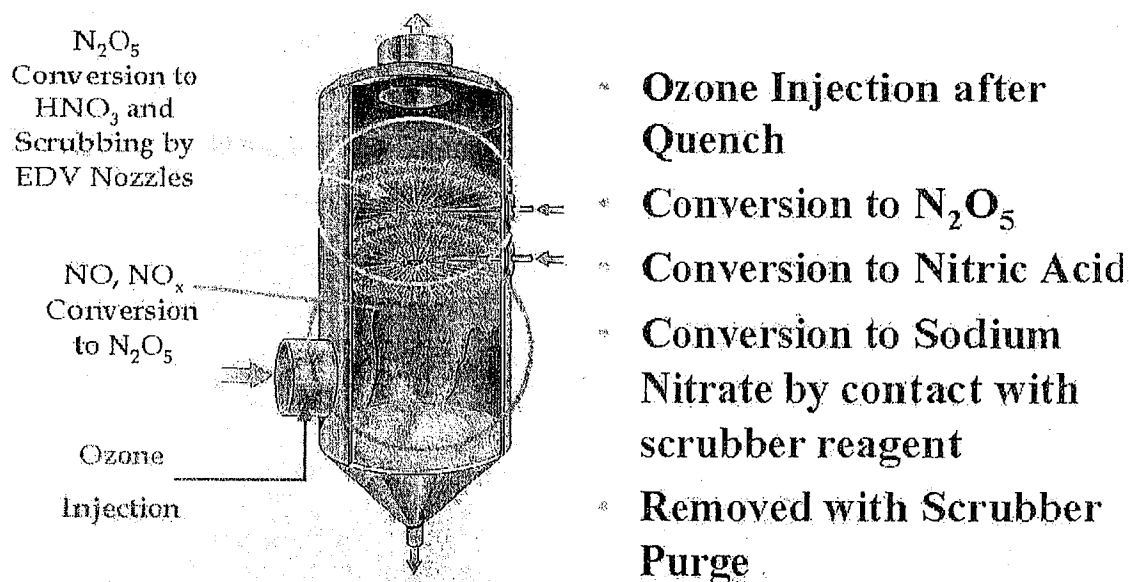
N$_2$O$_5$ Conversion to HNO$_3$ and Scrubbing by EDV Nozzles

NO, NO$_x$ Conversion to N$_2$O$_5$

Ozone Injection

- Ozone Injection after Quench
- Conversion to N$_2$O$_5$
- Conversion to Nitric Acid
- Conversion to Sodium Nitrate by contact with scrubber reagent
- Removed with Scrubber Purge

Figure 4-3.2. EDV Wet Scrubbing System with LoTOx^{TM} Injection

Potential applicability. The large gas volumes, high moisture levels and large quantities of dilution air needed to reach the operating temperature range in some systems may limit the applicability of the LoTOx^{TM} system.

Advantages. Table 4-3.1. provides an overview comparing the LoTOx^{TM} process w th SNCR and SCR technologies.

Table 4-3.1. Comparison Of Common Post Combustion NO_x Abatement Technologies For NO_x Emissions Control

	SNCR	SCR	LoTOx[TM]
Mode of Treatment	Reduction	Reduction	Oxidation
Active Chemical	NH_3 / Urea	NH_3 / Urea	Ozone
Gas Temperature Required °F	1650 – 2000	500 - 900	150 – 250
Pressure Required, psig	0+	0++	0+
Placement in Exhaust System	Near Combustion Chamber	Between Air Pre-Heater and Economizer (boiler)	Tail End
Catalyst Bed	No	Yes	No
Gas Phase Reaction Duct	Yes	No	Yes
Scrubber	Optional	Optional	Yes
NO_x Reduction Achieved	40 - 70 Percent	60 - 95 Percent	90 - 95 Percent
Slip of Active Agent	NH_3 – Yes	NH_3- Yes	Ozone - No
CO Emissions After Treatment	May Increase	May Increase	No Effect
SOx Emissions After Treatment	Little Effect – Maybe H_2S	Little Effect - Maybe H_2S	No Effect or Significantly Reduced
Gas Temperature Outside Operating Range - Overshoot	More NO_x Emissions Through NH_3 Oxidation	More NO_x Emissions Through NH_3 Oxidation, Ammonia Slip	Increased O_3 Consumption for the Time Period of Overshoot
Gas Temperature Outside Operating Range - Undershoot	More NO_x Emissions Through Reduced Reduction by NH_3	More NO_x Emissions Through Reduced Reduction by NH_3, Ammonia Slip	No Effect

An additional advantage is the control of SO_x emissions that would likely be achieved if the LoTOx[TM] system is added to any system that currently does not have a wet scrubber if joint control of SO_x and NO_x is required. Lower cost spray towers that do not appreciably control SO_x can be installed at lower cost than flue gas desulfurization scrubbers. The cost models for application of LoTOx at wet kilns are based on installing simple spray towers that do not control SO_x.

Disadvantages. It is likely that for most application the LoTOx[TM] option would be an add-on to existing APCD systems. Because of high electrical power usage costs are reported to be high. Electricity and oxygen costs alone are estimated to be greater than $1600/ton of NO_x controlled.

Additional nitrate captured in the existing sulfate scrubber could impact the quality of the plant's artificial gypsum although, with a typical dewatering system, this should not be a problem because of the much higher solubility of the nitrates relative to sulfates. High nitrate

wastewater could be used by local farmers as fertilizer or could be used at the plant to fertilize grass areas as well as water/fertilizer in quarry reclamation areas. Lowering the exit gas temperature and adding moisture may result in problems with condensation in the stack.

Emissions performance. There are three primary process variables which impact the NO_x control capabilities of $LoTOx^{TM}$ process: Temperature of the flue gas (T), Residence Time of the flue gas in the reactor duct (RT) and Amount of Ozone (O_3 Factors) injected into the reactor duct. Based on the results of the $LoTOx^{TM}$ demonstration testing, the most efficient control parameters for a full scale system on the Quemetco, Inc., furnace are a temperature of 175 °F or less, a residence time of four seconds, and an ozone injection factor of 80 to 90. The O_3 Factor represents the O_3 to NO_x ratio at the inlet to the reaction duct. The presented data uses O_3 Factor for the sake of clarity and to provide meaningful data while maintaining confidentiality of proprietary intellectual information. Figure 4-3.3. depicts the performance conditions of the $LoTOx^{TM}$ process for the design conditions of RT = 4 seconds, T = 175 °F and O_3 Factor = 70 to 90. Under these design conditions the NO_x removal achieved ranges from 80 percent at an O_3 Factor of 70 to 95 percent at an O_3 Factor of 90.

This technology should be considered transferable in nature. It has not been used on a cement kiln but it has been used on similar large sources. Discussions with this technology's vendors reveals that existing SOx and CO levels at the cement plants in Midlothian should no be a factor in the use of this technology. Applications or tests have already been performed at CO and SOx levels well above those seen in any of these cement plants.
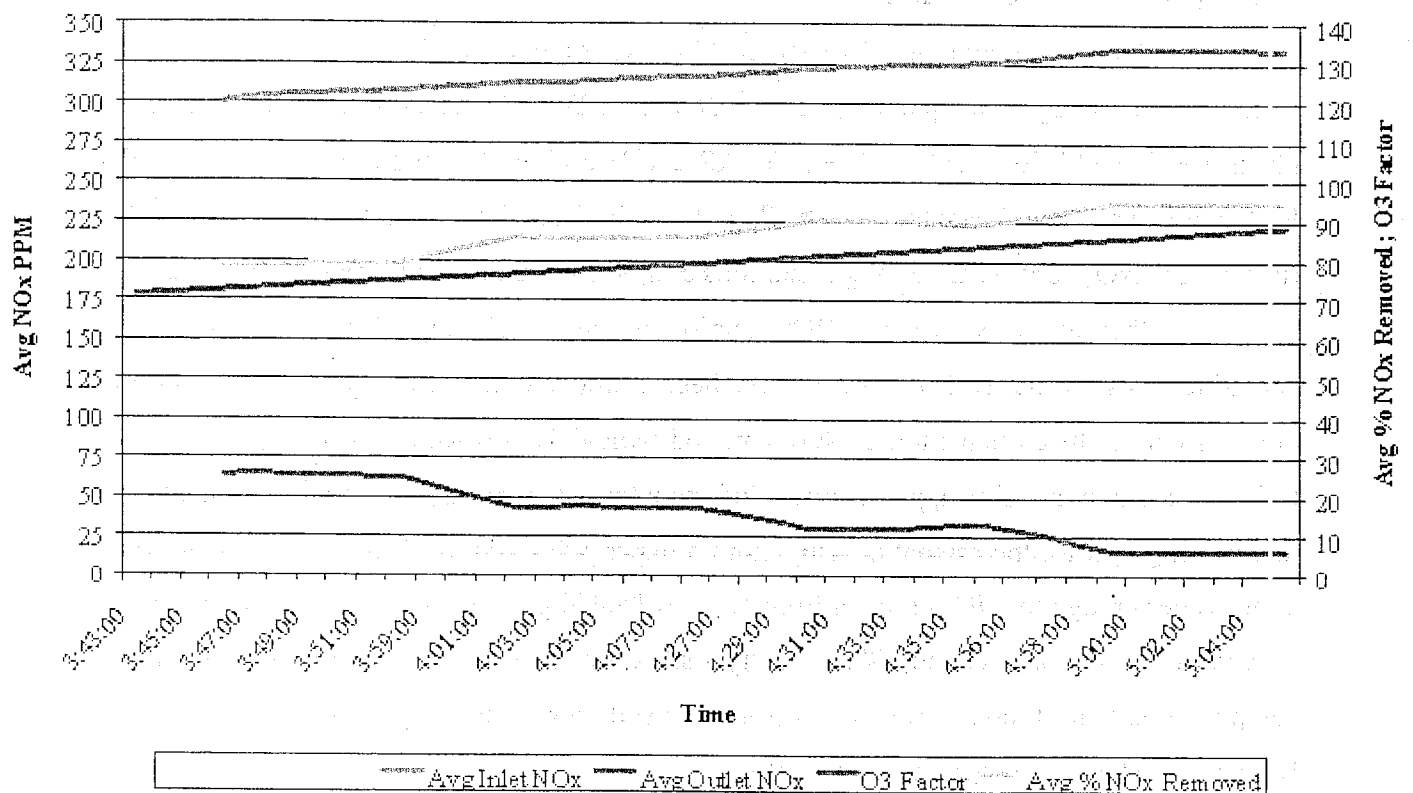
Ideal Operating Conditions for NOx Removal from 80% to 95%

Figure 4-3.3. Ideal Operating Conditions for NO$_x$ Removal from 80% to 95%

<u>Cost.</u> Ohio Coal Development Office (OCDO) provided 65 percent of the capital to install a $6.3 million LoTOx^{TM} unit at the Medical College of Ohio. The project includes two processes: LoTOx^{TM} for NO$_x$ and particulate material control and Rapid Absorption Process (RAP, another BOC licensed process) for sulfur dioxide control. The controls are for 25 megawatt capacity boilers burning Ohio coal containing 3 percent sulfur. According to the BOC

Company literature, the unit is designed to remove about 90 percent of the NO_x in emission gases. The RAP process uses a slurry of lime injected into the flue gas to capture SO_2 and a fabric filter (baghouse) to remove the calcium sulfate particles. Cost effectiveness has been estimated to be in the range of $1,700 to $1,950 per ton NO_x removed.[25]

In June 2001, BOC announced that they had installed, started up and commissioned a LoTOx[TM] unit at J & L Specialty Steel's Midland, PA plant. Details of the installation are sketchy. However, Robert Ferrell, BOC Vice President of Business Development, said, "We were able to modify the system to achieve a higher level of control than was originally anticipated. We have been able to reduce NO_x emissions by more than 95 percent.[26] No costs or capacity numbers were available.

A subsequent search of EPA's RBLC27 Database indicates that at least two other plants in the U.S. are using (or are planning to use) BOC's LoTOx[TM] process in their facilities. These plants are Lion Oil Company in El Dorado, AR and Marathon-Ashland Oil in Texas City, TX. Both plants use (or will use) the LoTOx[TM] on their Fluidized-Bed Catalytic Cracking Units (FCCU) for NO_x control. Operating conditions and performance results are not available.

Another article, written by a BOC employee, stated, "The capital (recovery) and operating costs for the (LoTOx) system have been evaluated for various system sizes and (they) fall well within the costs per ton of NO_x removed typical for post-combustion treatment technologies in non-utility applications." Unfortunately, this information is not very helpful for determining cost for the cement industry since a paper published by NESCAUM30 gives the cost effectiveness range for NO_x removal from $390 to $5,450 per ton NO_x. Cost effectiveness is heavily dependent on each individual facility's situation. This includes their existing control equipment, extent of modifications necessary to install new control equipment, and the degree of DRE required to achieve the desired results.

Based on the data available, capital costs for adding LoTOx[TM] to a system that does not have a wet scrubber such as the wet kilns in Midlothian are likely to be much more costly than the kilns that already have wet scrubbers. Vendor information was used to calculate costs associated with the application of LoTOx to the cement plants in Midlothian. Estimated costs associated with the precalciner kilns which already have scrubber systems in place are $2300-$2600/ton of NO_x controlled. Estimated costs associated with the wet kilns which do not have scrubber systems in place are $3000-$3700/ton of NO_x controlled. The costs for the wet kilns

include installation of a spray tower to remove the soluble NO_x oxidation products produced by the LoTOx system.

4.3.3 Hydrogen Peroxide

General description. There are several methods for controlling NO_x emissions. Gas scrubbing is one of the most common forms of NO_x treatment, with sodium hydroxide being the conventional scrubbing medium. However, the absorbed NO_x is converted to nitrite and nitrate, which may present wastewater disposal problems. Scrubbing solutions containing hydrogen peroxide are also effective at removing NO_x, and can afford benefits not available with NaOH. For example, H_2O_2 adds no contaminants to the scrubbing solution and so allows commercial products to be recovered from the process, e.g., nitric acid or nitrate salts (for use as fertilizer). In its simplest application, H_2O_2 (0.5-1 wt.%) and nitric acid (35-45 wt.%) are used to scrub both nitric oxide (NO) and nitrogen dioxide (NO_2) -- the chief components of NO_x from many industrial sources. The reactions are rapid at moderate temperatures (30-80 °C), with about 1.7 and 0.37 lbs H_2O_2 required per lb NO and NO_2, respectively. The chemistry controlling the process is outlined below:

$$3NO_2 + H_2O <==> 2HNO_3 + NO$$

$$NO + HNO_3 + H_2O ----> 3HNO_2$$

$$HNO_2 + H_2O_2 ----> HNO_3 + H_2O$$
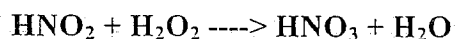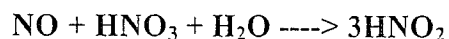
There are several other processes that also use hydrogen peroxide to remove NO_x. The Kanto Denka process (1) employs a scrubbing solution containing 0.2% hydrogen peroxide and 10% nitric acid while the Nikon process uses a 10% sodium hydroxide solution containing 3.5% hydrogen peroxide. A fourth process, the Ozawa process, scrubs NO_x by spraying a hydrogen peroxide solution into the exhaust gas stream. The liquid is then separated from the gas stream, and the nitric acid formed is neutralized with potassium hydroxide. The excess potassium nitrate is crystallized out, and the solution reused after recharging with hydrogen. In addition to the methods cited above in which NO_x is oxidized to nitric acid or nitrate salts, a series of Japanese patents describe processes and equipment for reducing NO_x to nitrogen using hydrogen peroxide and ammonia (3, 4, 5, 6). The processes are efficient but must be carried out at higher temperatures than the processes cited earlier.

The injection of hydrogen peroxide (H_2O_2) into hot flue gases to prevent emissions of nitrogen oxides (NO_x) has been demonstrated at the pilot scale at a boiler at Kennedy Space Center (KSC). That project was an outgrowth of research funded by the GCHSRC from the years 1993-1996. The H_2O_2 is injected into hot boiler flue gases to oxidize the NO into NO_2, HNO_2 and HNO_3, which can then be removed in a wet or dry scrubber (see Figure 4-3.4.).
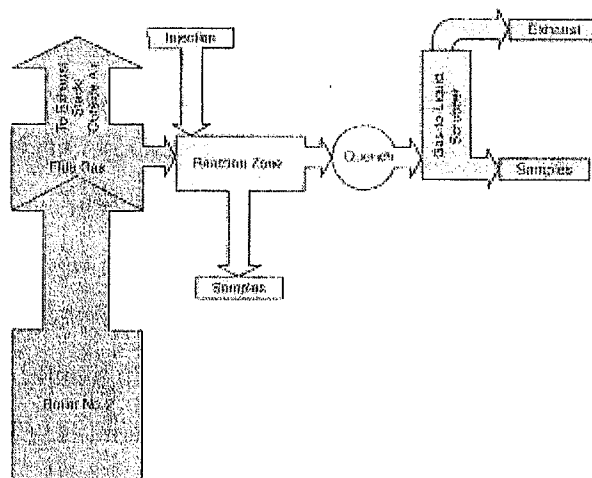

Figure 4-3.4. Conceptual Design of Hydrogen Peroxide NO_x Control System

In one of several sets of experiments to demonstrate the feasibility of the method, the optimum temperature for conversion of NO to HNO_2, HNO_3, and NO_2 by use of injected H_2O_2 was found to be about 500 °C (see Figure 4-3.5.).
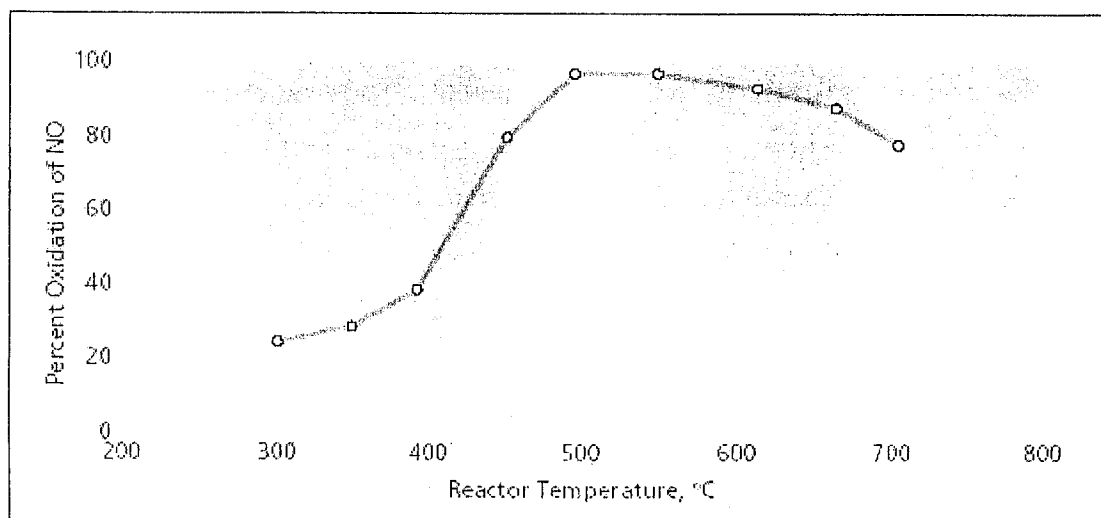

Figure 4-3.5. The conversion of NO by oxidation to other species was measured as a function of reactor temperature. The reactor inlet conditions for the points shown here were 400 ppm NO and 400 ppm H_2O_2 for a molar ratio of 1:1.

A study performed under the guidelines of the EPA, EPRI comparing the economics of SCR and the experimental H_2O_2-injection/scrubbing method was conducted for a design base case and a variety of alternative cases. This study illustrated the tradeoff between capital and operating costs for the two methods. The single largest factor in determining the total cost of one method relative to the other method was found to be the H_2O_2:NO molar ratio. At the H_2O_2:NO molar ratio of 1.92, which was previously demonstrated in the laboratory, the H_2O_2-injection/scrubbing method was shown to be uneconomical. However, it was also concluded that the molar ratio in a full-size coal-fired power plant could be lower than that found in the laboratory, and that on the basis of all the assumptions of the study, at an H_2O_2:NO molar ratio of 1.37, the H_2O_2 injection/scrubbing method could be an economically feasible alternative to SCR.

Pilot-scale tests run at Kennedy Space Center demonstrated the feasibility and competitiveness of this new technology. The H_2O_2 to NO molar ratio, at 500 °C shown to achieve a NO conversion efficiency of > 90 percent was 1:1, which is significantly lower than the required 1.37:1 (See Figure 4-3.6.).
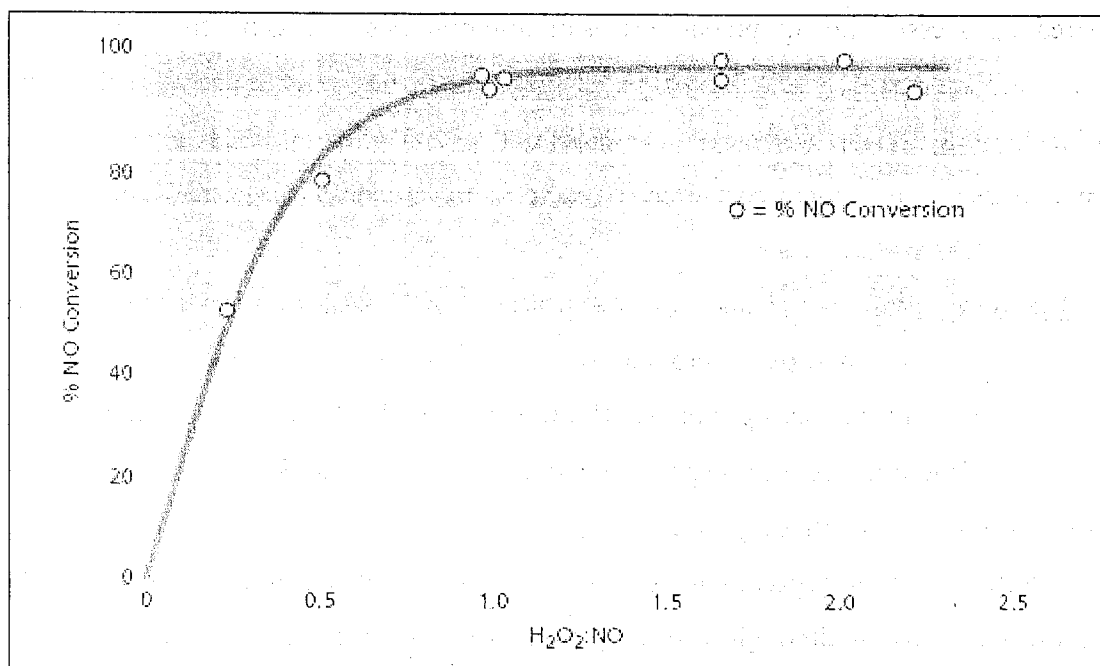

Figure 4-3.6. The outlet concentration of the O was significantly reduced when the H_2O_2 was injected. At 500 °C, 400 ppm NO, and various inlet concentrations of H_2O_2 (represented as the molar ratios), 90 percent conversion of NO was achieved at the reactor outlet for a molar ration of 1:1.

Potential applicability. This option is a solution that may have particular applicability to kilns with existing scrubber systems. Data gathered suggests it may work over a wide range of temperatures depending on the specific version of this technology that is implemented. For he high temperature version of this process, injection of the hydrogen peroxide into the upper portion of the preheater tower of a precalciner kiln at the appropriate temperature may be possible.

Advantages. The biggest advantage of this technology may be a relatively low capital investment for plants with existing scrubbers. An additional advantage is that there are indications that hydrogen peroxide based scrubbers may also enhance SO_x scrubbing and may lower hydrocarbon emission depending on the operating temperature, reagent system and retention time of the system.

An additional advantage of this technology is that it operates in a unique temperature window that is slightly below the temperatures commonly used for SCR. The optimal technology for any specific cement kiln process may be the technology that installs best in the existing temperatures windows of the process with the least potential adverse impact on downstream processes and equipment. Prices of ammonia-based reagents fluctuate with natural gas prices and are currently relatively high. Cement plants may elect to use more than one NO_x control technology to take advantage of changes in the market for reagents. Hydrogen peroxide currently appears to be a more cost effective reagent than ammonia-based reagents.

Disadvantages. For plants without scrubbers, add on systems are required. An additional factor is that the cost of hydrogen peroxide has risen significantly in recent years with increased natural gas prices and fluctuating supplies. Hydrogen peroxide has become a major commodity chemical as a bleaching agent for paper production free of chlorine. Recent production capacity increases appear to be stabilizing prices.

Additional nitrate captured in the existing sulfate scrubber could impact the quality of the plant's artificial gypsum although, with a typical dewatering system, this should not be a problem because of the much higher solubility of the nitrates relative to sulfates. High nitrate wastewater could be used by local farmers as fertilizer or could be used at the plant to fertilize grass areas as well as water/fertilizer in quarry reclamation areas.

Emissions performance. At 500 °C and with a molar ratio of 1:1 H_2O_2/NO_x removal efficiencies of greater than 80% appear to be achievable. Scrubber efficiency data for the wet low temperature process was not available. Either of these technologies should be considered investigative in nature. Application of this technology would clearly be an innovative approach that does not have a history of commercial application compared to SCR, SNCR or LoTOx. Testing in a cement plant application would clearly be required to determine performance and process impacts.

Cost. Assuming a cost of $0.50/lb of hydrogen peroxide the reagent cost would be approximately $739/ton of NO_2 removed (depending on the existing oxidation state of the NO in the system). This might be offset to some extent by the sale of solutions of nitrate salts as fertilizer. This cost appears to be favorable relative to the electrical and oxygen costs of the LoTOx^{TM} that exceed $1600/ton of NO_x controlled. It is also favorable to the current ammonia cost of about $1200/ton of NO_x controlled using SNCR.

4.3.4 OXONE (Dupont – potassium monopersulfate)

General description. Scrubbing with strong aqueous oxidants promises to be less expensive than competing post-combustion methods for NO_x removal such as selective catalytic reduction (SCR) and thermal NO_x removal. The goal of a project by Yusuf G. Adewuyi at North Carolina A&T State University is to develop an innovative and cost-effective aqueous scrubber for the simultaneous removal and destruction of oxides using strong oxidizing agents such as oxone. Oxone ($2KHSO_5.KHSO_4.K_2SO_4$) is a triple salt of potassium and may be regarded as a mono-substituted derivative of hydrogen peroxide. However, it has an oxidation potential greater than that of hydrogen peroxide (E HSO_5^-/HSO_4^- = 1.82 eV compared to E H_2O_2/H_2O = 1.77 eV). The aqueous absorption and kinetics of oxidation of nitrogen oxides (NO_x) and SO_2 by OXONE in a bubble column operated as batch or continuous OXONE was presented at an AIChE meeting in October of 2005. Table 4-3.2. provides a breakdown of the chemical constituents of the Oxone reagent.

Table 4-3.2. Oxone Constituents

Material	CAS Number	%

"Oxone" Monopersulfate Compound	70693-62-8	
Potassium Peroxymonosulphate	10058-23-8	34-43
Potassium Bisulfate	7646-93-7	18-23
Potassium Sulfate	7778-80-5	23-29
Potassium Peroxydisulfate	7727-21-1	2-3
Sodium Carbonate	497-19-8	0-20
Magnesium Carbonate	546-93-0	1-2

Potential applicability. Applicability is similar to the wet low temperature hydrogen peroxide option.

Advantages. Advantages are similar to the hydrogen peroxide option. Costs may be lower.

Disadvantages. This is an experimental technology. Additional nitrate captured in the existing sulfate scrubber could impact the quality of the plant's artificial gypsum although with a typical dewatering system this should not be a problem because of the much higher solubility of the nitrates relative to sulfates. High nitrate wastewater could be used by local farmers as fertilizer or could be used at the plant to fertilize grass areas as well as water/fertilizer in quarry reclamation areas.

Emissions performance. As an experimental technology performance is not clear but is likely to be similar to the hydrogen peroxide technology. This technology should be considered investigative in nature.

Cost. Oxone is a commercial product manufactured by Dupont. Inquiries to Dupont about cost have not been responded to at this time.

4.3.5 ███████████

██

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Table 4-3.4. Summary of Modeling Results for LoTOx on Ellis County Kilns – Performance Results

Existing Unit	Control Technology	Emissions Rate tpy before	Emissions Rate tpy after (a)	Controlled Emissions Rate ppm	Controlled Emission Rate lb/tonne clinker	Control Efficiency %	Reduction tpy

h) NOx emission rate after SCR does not reflect SCR efficiency reduction due to adjustment by the ozone season fac or of 0.671 (NOx reduction is modeled to occur only during the ozone season).

j) Models assume mid-kiln firing installed at TXI as required under current SIP.

Table 4-3.5. Summary of Modeling Results for LoTOx on Ellis County Kilns – Economic Results

Existing Unit	Control Technology	Capital Cost	Annual Cost	Cost Effectiveness $/ton NOx	Energy Penalty or Benefit	Emissions Penalty or Benefit	Burden Cost $/tonne clinker

a) Increased fan power due to pressure drop across scrubber included in the models

c) Costs for wet kilns include addition of spray tower to scrub oxidation products.

4.4 Process Modification

Process modifications are applicable to any type of kiln and are usually done to reduce heat consumption, to improve clinker quality, and to increase the lifetime of the equipment (such as the refractory lining) by stabilizing process parameters. Reduction of emissions, such as NOx, SOX, and dust, are secondary effects of these modifications. Smooth and stable kiln operation close to design values for process parameters is beneficial for all kiln emissions. Process modifications can include many elements, such as instruction and training of the kiln operators, homogenizing raw material, ensuring uniform coal dosing, improving the cooler's operation, and installing new equipment. Process modifications are primarily done to reduce operating costs, increase capacity, and improve product quality. Adopting process modifications usually results in a reduction of operating costs for a kiln. The savings result from reduced fuel and refractory consumption, lower maintenance costs, and higher productivity, among other factors[1]

This section describes process modifications that improve fuel efficiency and kiln operational stability with an emphasis on reducing NOx formation. Since NOx formation is directly related to the amount of energy consumed in cement-making, improving fuel efficiency and productivity will reduce NOx emissions.

4.4.1 Combustion Zone Control of Temperature and Excess Air

Continuous monitoring of O_2 and CO emissions in the cement kiln exhaust gases indicates the amount of excess air. At a given excess air level, NOx emissions increase as the temperature of the combustion zone increases. A typical kiln combustion zone solids temperature range is about 1430 to 1540°C (2600 to 2800°F) for completion of clinkering reactions and to maintain the quality of the cement produced.[2] The corresponding gas-phase temperature is usually greater than 1700°C (3100°F).[3] Maintaining the combustion zone temperature at a necessary minimum value would minimize both the process energy requirement and the NOx emissions.

Along with the appropriate temperature, it is also necessary to maintain an oxidizing atmosphere in the clinker burning zone to ensure the quality of the clinker produced. Although a kiln could be operated with as little as 0.5 percent kiln exhaust oxygen level, typically the kiln operators strive for an oxygen level of 1 to 2 percent to guarantee the desired oxidizing conditions in the kiln burning zone. An experimental test on a cement kiln showed that by

[Text redacted]

4.4.4 Kiln Fuel

Changing the primary kiln fuel from natural gas to coal can reduce the flame temperatures significantly, resulting in lower thermal NOx emissions.[10,11] Although nitrogen present in coal may provide greater fuel NOx contribution, switching the fuel burned in kilns from natural gas to coal has been shown to provide substantial reduction in the total NOx emissions in one experimental study.[10] In the dry process kilns tested in this study the average NOx emissions decreased from 20.4 lb/ton of clinker to 6.2 lb/ton of clinker when the fuel was changed from natural gas to coal. A number of cement kilns have already made the switch from natural gas to coal and currently 87 percent of cement kilns in the United States use coal as the primary fuel.[12]

When natural gas (with no nitrogen in the fuel) is used in the burning zone of a cement kiln, the NOx emissions are significantly higher than when coal is used. There may be additional environmental impacts when coal is burned as opposed to natural gas (e.g., sulfur dioxide and

sulphate emissions may increase). Although switching to a lower nitrogen fuel in a precalciner may reduce NOx, the fuel nitrogen content in the burning zone has little or no effect on NOx generation. Some researchers have found no relationship between fuel nitrogen content and the NOx emissions from a cement kiln.[13]

Switching to a fuel with a higher heating value and lower nitrogen content may reduce NOx emissions in a cement kiln, e.g., petroleum coke has a lower nitrogen content per million Btu than coal. Petroleum coke is also more uniform in terms of heat value, lower in volatile matter content and burns with a lower flame temperature. However, petroleum coke cannot be burned alone because it does not provide enough volatile matter.[14]

4.4.5 Increasing Thermal Efficiency

The thermal efficiency of the cement-making process has improved substantially as energy costs have increased and new technology has been developed. Although there are a variety of cement process technologies used in the US, the kilns in this study are all either 1960's wet kiln technologies that are not energy efficient or modern dry process kilns with preheat and precalcination that represent the most energy efficient process for making Portland cement. Both Holcim #2 and TXI #5 are new and energy efficient units. ████████████████████ ███ ████████████████████████. In addition, there are interim steps that improve the efficiency of wet process to semi-wet or semi-dry process. However, the main opportunity for substantial reductions in NOx emissions in Ellis County from energy improvements comes from closing the wet process units and replacing them with modern, dry-process production.

Calciner Modifications

A study for the Department of Energy (Worrell 2004) reports evaluates use of low pressure drop cyclones for suspension preheaters. Worrell reports: "Cyclones are a basic component of plants with pre-heating systems. The installation of newer cyclones in a plant with lower pressure losses will reduce the power consumption of the kiln exhaust gas fan system. Depending on the efficiency of the fan, 0.6-0.7 kWh/ton clinker can be saved for each 50 mm W.C. (water column) the pressure loss is reduced. For most older kilns this amounts to savings of

0.6-1.0 kWh/ton (Birch, 1990). Fujimoto (1994) discussed a Lehigh Cement plant retrofit in which low-pressure drop cyclones were installed in their Mason City, Iowa plant and saved ᴢ kWh/ton clinker (Fujimoto, 1994). Installation of the cyclones can be expensive, however, since it may often entail the rebuilding or the modification of the preheater tower, and the costs are very site specific. Also, new cyclone systems may increase overall dust loading and increase dust carryover from the preheater tower. However, if an inline raw mill follows it, the dust carryover problem becomes less of an issue. A cost of $2.7/annual ton clinker is assumed for a low pressure drop cyclone system."

Semi-Wet Upgrades to Wet Kilns

Hendriks and Worrell (Hendriks 1998) report that conversion from a wet to a semi-wet process can save between 0.8 and 1.6 GJ/ton of clinker. There is a penalty of increased electrical energy use associated with this conversion of approximately 3 to 5 kWh.

Worrell (Worrell 2004) also reviews this option and describes it as a filter press system. "In the wet process the slurry typically contains 36% water (range of 24-48%). A filter press can be installed in a wet process kiln in order to reduce the moisture content to about 20% of the slurry and obtain a paste ready for extrusion into pellets (COWIconsult et al., 1993; Venkateswaran and Lowitt, 1988). In the U.S. several plants have tried slurry filters, but have not been very successful. Currently, there seem to be no plants in the U.S. using this technology (Young, 2002). Additional electricity consumption is 3-5 kWh/ton clinker (COWIconsult et al., 1993). In this analysis it is assumed that energy use increases by 4 kWh/ton clinker to reduce the moisture content to 20%. The corresponding fuel savings are 1.0 MBtu/ton (COWIconsult et al., 1993). Jaccard and Willis (1996) estimate the conversion cost to run $1.6/annual ton clinker capacity with increased operation costs of $0.1/ton clinker (Jaccard and Willis, 1996)."

Semi-Dry/Semi-Wet Upgrades to Wet Kilns

Hendriks and Worrell (Hendriks 1998) report that conversion from a wet to a semi-dry process can save approximately 2.0 GJ/ton of clinker. They report a "small" increase in electrical energy use associated with this conversion of approximately 3 to 5 kWh.

Buzzi-Unicem operates a semi-dry/semi-wet system in Greencastle, IN, which had been converted from a large wet kiln system. While anticipated increases in production capacity were achieved predicted improvements in thermal efficiency were not fully realized. Actual thermal efficiency improvement was only about 15%. Capital cost for this type of conversion are likely to be in the range of $75-85/tonne. Significant NOx improvements have been observed in this conversion although not to the levels predicted by the vendor. Even with a 50% increase in production total NOx emissions have been significantly reduced.

Because kiln conversion economics are significantly impacted by the size of the exiting kiln the conversion of any of ▉▉▉▉▉▉▉▉▉▉▉▉▉▉▉▉▉▉ is not considered a feasible alternative for further analysis.

Replacement of Wet Kilns with Dry

Worrell evaluates conversion of a wet kiln to a dry preheat/precalciner process (Worrell 2004). This conversion is essentially a reconstruction of the main kiln and processing areas with a new, modern dry plant. Worrell reports "If economically feasible a wet process kiln can be converted to a state-of-the art dry process production facility that includes either a multi-stage preheater, or a pre-heater/pre-calciner. Average specific fuel consumption in U.S. wet kilns is estimated at 6.0 MBtu/ton clinker. Studies of several kiln conversions in the U.S. in the 1980s found fuel savings of 2.9 MBtu/ton or less (Venkateswaran and Lowitt, 1988). In Hranice (Czech Republic) a 1,050 tonne per day wet process plant was converted to a dry kiln plant with a new kiln specific fuel consumption of 2.7 MBtu/ton clinker (Anon., 1994b). Fuel savings of 2.7 MBtu/ton clinker and an increase in power use of about 9 kWh/ton clinker (Vleuten, 1994) are assumed. The cost of converting a wet plant to a dry process plant may be high, as it involves the full reconstruction of an existing facility. Costs may vary between $50/annual ton clinker capacity and $100/annual ton clinker capacity (van Oss, 1999; Nisbet, 1996)."

This options is also discussed by Hendriks (Hendriks 1998). Hedriks gives a cost of approximately $133/ton of annual capacity as the cost of building the new dry process plant. Hedriks estimates that about 2.2 GJ/ton of energy can be saved. Increased energy use of about 10kWh/ton is required for operation of the preheat/precalcination tower.

Wet to Dry Conversion of Ellis County Kilns

On average, dry preheat/precalciner kilns emit substantially less NOx per tonne of cement produced and require about less energy per tonne of cement produced. Both in terms of energy use and NOx emissions rates, the wet process units are often nearly double the modern dry process units. The cost modeling presumed that the wet kilns could obtain a value approximately that of high performing modern kilns and that would result in an approximate 65% decrease in NOx emissions. A substantial energy savings was predicted to result in fuel savings in the cost models (see Confidential Attachment Wet to Dry Conversions).

The economics of wet kilns compared to dry kilns are very complex and involve issues such as lower production capacity of wet kilns, use of waste fuels and quality of cement products. However, as the energy costs of wet production are higher than for modern dry process units, there is a point at which the higher costs of pollution controls that may result from the final determinations of this study would trigger a decision to close the wet kilns and replace them with dry. Stating this another way, it is likely that at a certain cost of pollution controls in terms of dollars per tonne of clinker produced, the economics of the wet process including higher fuel costs and higher pollution control costs would reach a point where replacement of the wet units with larger dry process units would be the reasonable alternative for a cement plant to continue operations at that site.

It is likely that any new kilns built to replace the wet kilns in Ellis County would include increased production capacity in the economic justification. However, for the purposes of control cost modeling, the units need to replace the existing capacity for the evaluations to make sense in the context of our control option evaluations. For this reason, two dry process kiln replacement scenarios were modeled

The modeling, summarized in Table 4-15, shows an annualized cost of approximately $11 per tonne of clinker for the replacement dry process units. This cost includes an annual benefit of approximately $4.0 to $4.5 million in reduced fuel costs used as the fuel. An increased annual cost of electricity of approximately $0.5 million results from the additional fan power required to move air through the preheat and precalcination tower. This information indicates that energy savings are very significant, but are not sufficient for a company to justify replacement of the wet kilns. Annual operating costs (capitalization of the new equipment) are reduced by nearly one third to approximately $9 million dollars by energy savings; however, even with the current high costs of energy this would not by itself justify replacement of the wet kilns.

The current use of alternative fuels complicates this analysis. The fuel savings are based on an assumption that the energy for the current wet kilns is all based on coal Lower costs alternative fuels lessen the economic benefit of the increased energy efficiency. Preserving these alternative fuel programs may be important economic considerations in company analyses cf wet to dry conversions and the overall economics of cement production on a dollars per tonne o' clinker basis. ██ ██ ██. If we assume that the current amount of alternative fuels are permitted to be used in a new larger kiln, the amount of coal predicted to be reduced would still be reflected in the overall reduction in fuel use.

Conversion of the Ellis County wet kilns to dry process would result in year-round emissions reductions for NOx, SO_2, particulate matter and hazardous air pollutants. The modern dry process unit would have updated controls that would result in a potentially large emissions reduction credits for SO_2 that could be marketable depending on how this overall project was viewed under Texas regulations. If this emissions reduction was creditable and marketable, this would provide some additional benefit to this approach.

Table 4-4.3. Summary of Modeling Results for Wet to Dry Conversion of Ellis County Kilns – Performance Results

Existing Unit	Replacement Unit	Emissions Rate tpy before	Emissions Rate tpy after	Controlled Emissions Rate ppm	Controlled Emission Rate lb/tonne clinker 2.0 lbs/ton clinker	Control Efficiency %	Reduction tpy
▮	▮	▮	▮	▮	▮	▮	▮
▮	▮	▮	▮	▮	▮	▮	▮

Table 4-4.4. Summary of Modeling Results for Wet to Dry Conversion of Ellis County Kilns – Economic Results

Existing Unit	Replacement Unit	Capital Cost	Annual Cost	Cost Effectiveness $/ton NOx	Energy Penalty or Benefit*	Emissions Penalty or Benefit**	Burden Cost $/tonne clinker
▮	▮	▮	▮	▮	▮	▮	▮
▮	▮	▮	▮	▮	▮	▮	▮

* large benefit in fuel efficiency partly offset by increased electrical use in tower
** large benefit in reduced fuel – does not account for increased emissions at power plant for power used in tower.

Table 4-4.5 Summary of Modeling Results for Calciner Upgrade for Ellis County Kilns – Economic Results

Control Technology	Control Technology Status	Emissions Rate before control tpy	Emissions Rate before control lbsNOx//tonne	Percent Control	Emissions Reduction from Control tpy	Controlled Emission Rate lbNOx/tonne	Cost Effectiveness $/ton NOx	Burden Cost $/tonne clinker
███████	████████	█████	█████	█████	█████	██	██████	█████

40% for new low-NOx calciner based on TXI #5 performance.
Cost effectiveness for calciner upgrade calculated by ratio of burden costs using SCR data.
Calciner upgrade is not a seasonal ozone measure – emissions benefit is for full year.

References:

Worrell, Ernst and Galitsky, Christina, "Energy Efficiency Improvement Opportunities for Cement Making An ENERGY STAR Guide for Energy and Plant Managers", Energy Analysis Department, Environmental Energy Technologies Division., Ernest Orlando Lawrence Berkeley National Laboratory, University of California, January 2004

Hendriks, C.A., E. Worrell, D. de Jager, K. Blok, and P. Riemer. 1998. Emission Reduction of Greenhouse Gases from the Cement Industry Lawrence Berkeley National Laboratory, Berkeley, California. IEA Website http:/www.ieagreen.org.uk/jan46.htm

4.5 Performance of Current NO$_x$ Control Techniques and Technologies in the Cement

4..5.1 Summary of Current Performance of NO$_x$ Control Technologies

See Table 4.5.1.

4..5.2 Summary of Current Regulations

This report focuses on evaluating the NO$_x$ control measures for Portland cement manufacturing that go beyond current TAC Chapter 117 requirements. In the US, it appears that several areas of the country are in a similar position to Texas in that they are currently evaluating more stringent active controls of NO$_x$ for ozone attainment under the 8-hour standard. While active NO$_x$ controls may be required under New Source Review requirements, current State SIP requirements are less stringent.

Control requirements in Europe are generally moderately stringent emissions limitations based on a performance requirement such as 500 mg/m3 . These requirements have prompted use of SNCR (recent documents report as many as 50 installations), but generally are not stringent enough to require higher performing technologies. One exception is Sweden, that has a very stringent performance requirement of 200 mg/m3 (approximately 98 ppm). There are currently two cement plants in Europe capable of meeting this 200mg/m3 limit. The Solnhofer Portlandzementwerke in Germany (using SCR) and Scancem Slite in Sweden (using SNCR with multi-point injection).

As noted above, the US is somewhat behind Europe in requiring active controls on Portland cement manufacturing plants. A recent memo from EPA Region 6 indicates that recent BACT determinations typically require 1.95 lbs/ton of clinker (2.15 lbs/tonne) and SNCR. Other recent US studies include planning studies for compliance with the 8-hour ozone standard.

Two recent documents that recommend measures beyond current TAC Chapter 117 requirements are the Midwest Regional Planning Organization's "Identification and Evaluation of Candidate Control Measures, April, 2005" and the "Fall Line Air Quality Study. November, 2004". Both of these studies recommend consideration of SCR for control of cement kilns.

TABLE 4.5.2. National SO2 and NO$_x$ emission limits for the production of cement within the European Union (EU 15), in mg/Nm3, around 2000

Country	Data based on	New/modified or existing plant	SO2 normal situation	SO2 S-rich raw materials	NOx	PCDD/Fs* ng TEQ/Nm3
Austria	Na a)	new/modified existing	200 200	400 400	500 1000	
Belgium	P	new/modified existing	1000 1000		1800 1800	
Denmark	P a)	Existing	5/250/450b)	no limit	1200/2500/850c)	no limit
Finland	P d)	Existing	150–400		1200–1800	
France	Na	new/modified existing	500 500e)	1200/1800f) 1200/1800e)f)	1200/1500/1800g) 1200/1500/1800g)	
Germany	Na	new/modified existing	400 400	400 400	500 800	
Greece						
Ireland	Na	new/modified existing	400 400	700 700	1300 1300	n.a. n.a.
Italy	Na/P	new/modified existing	600		1800	1000Ch) 1000Ch)
Luxembourg	P	existing	100i)		800j)	0.1k)
Netherlands	P	existing	l)		1300j)	0.1
Portugal	Na	new/modified existing	400	1300		0.1 0.1
Spain	Na	new/modified existing	2400/6000m) 600n) 2400/6000m) 600n)	2400/6000m) 1800n) 2400/6000m) 1800n)	1300-1800n)	
Sweden	P	existing	-	<200	<200	0.1
UK	Na o)	new/modified existing	200p)q)	600-2500r)	900p) 500-1200q)s)	

Na = National law; R=Regional law; P=Typical permit; in mg/ Norm m3.
* Polychlorinated dibenzo dioxins and furans (total emitted quantity in nano g/ Norm m3).
a) Daily averages and reference condition of 273 K, 101.3 kPa, dry gas and 10% O2.
b) 5 for semi-dry process, 250 for wet process and 450 for wet process with wet scrubber and heat recovery. Limits under discussion.
c) 1200 for semi-dry process, 2500 for wet process and 850 for wet process with wet scrubber and heat recovery. Limits under discussion.
d) Monthly averages, reference condition of 10% O2 and dry gas.
e) Existing plant must meet limit for new plant by 2001.
f) 1200 mg/Nm3 if ≥200 kg/h; 1800 mg/Nm3 if < 200 kg/h.
g) 1200 mg/Nm3 for dry process with heat recuperation, 1500 mg/Nm3 for semi dry and semi wet processes, and 1800 mg/Nm3 for wet and dry processes without heat recuperation.
h) General rule for any kind of industrial emission.
i) Half hour average.
j) Daily average value.
k) 6 hour average.
l) 90 kg/h as daily average, maximum 375 tonne/year.
m) Current limits.
n) Limits under discussion.
o) IPC Guidance Note S2 3.01.

Japan has national standard for NO_x from cement plants and divides the emissions limits into those that apply to plants built before 1975 and those built after 1975. For pre-1975 plants the NO_x standard is 480 ppmv and for those built after, the standard is 250 ppmv. The 250 ppmv standard is very similar to the German standard of 500 mg/m3.

The Fall Line Study was conducted for the State of Georgia and recommends SCR for wet kilns as well as dry process kilns and provides estimates of cost effectiveness per ton of NO_x controlled. The Midwest RPO Study also discusses the potential for control of wet kilns with SCR, particularly for low-dust applications (after pollution controls) and mentions the high cost of gas reheat as a limitation in application of this technology. SCR costs are only estimated for long dry and dry preheat/precalcination process kilns.

Table 4.5.3. Midwest RPO – LADCO Study
Large Preheater Kiln SCR 1200000 tpy clinker 2880 tpy uncontrolled emissions

	70% Removal Efficiency		90% Removal Efficiency	
	Low Capital Cost	**High Capital Cost**	**Low Capital Cost**	**High Capital Cost**
Total Capital Investment – TCI	$1,760,296	$14,668,188	$1,760,296	$14,668,188
Total Annual Cost	$1,305,377	$3,040,107	$1,305,377	$3,040,107
Pollutant Removal - tpy	2,016	2,016	2,592	2,592
Cost Per Ton of NOx Removed	$648	$1,508	$504	$1,173

TABLE 4.5.4. Fall Line Air Quality Study (Georgia)				
Medusa Cement (Houston)	In-process fuel use – coal	SNCR	$1,726	
	Cement manufacturing dry	Mid-kiln firing	$62	

	Cement manufacturing wet	Mid-kiln firing	$62	
		SCR	$3,947	Mid-kiln

In summary, current US emissions limitations indicate that 1.95 lbs/ton of clinker using SNCR is currently considered BACT for dry kilns. In order to meet 8-hour ozone standards, several areas of the country are looking at requiring more stringent NO_x controls on Portland cement plants and at least two areas are looking at requiring SCR. Experience in Europe indicates that emissions levels of approximately 200mg/m3 (98 ppm) and less than 1.0 lb/tonne of clinker are being achieved at two dry precalciner kilns, one using SNCR and one using SCR.

4.5.3 Summary Of European Experiences

In Europe, many cement plants have adopted general primary measures, such as process control optimization, use of modern, gravimetric solid fuel feed systems, optimized cooler connections and use of power management systems. These measures are usually taken to improve clinker quality and lower production costs but they also reduce the energy use and air emissions.[1]

In March 2000, the European Integrated Pollution Prevention and Control (IPPC) Bureau issued a report on Best Available Techniques for European cement kilns.[1] The report collected emissions data from several sources. Emission rates for European kilns included in this study range from less than 0.8 to 12 lb NO_x /ton of clinker. A set of German kiln emission measurements presented in the European report found NO_x emissions for a cyclone preheater with heat recovery of 1.2 to 6.2 lb/ton of clinker, for a cyclone preheater without heat recovery of 1.6 to 7.0 lb/ton of clinker, and for a grate preheater of 1.6 to 8.2 lb /ton of clinker. These rates are similar to the averages for preheater and precalciner kilns found by EC/R in the new data presented in Chapter 4 (1.7 and 2.7 lb/ton of clinker respectively), but are less than those reported in the ACT document (5.9 and 3.8 lb/ton of clinker respectively).[1]

Table 4-5.5. presents a summary of NO_x control device applicability, reduction efficiency, and reported average emissions from the IPPC Bureau report on BAT for European cement kilns.[1] There are no emissions data in the IPPC report for kilns with CemStar technology or midkiln firing. For low- NO_x burners, the IPPC report found a lower average NO_x emissions rate (1.6 lb/ton of clinker) than EC/R found in the new State data (8.98 lb/ton of clinker). Both

the IPPC report and the 1994 ACT document had estimated reduction efficiencies for low- NO_x burners of up to 30 percent. The reduction efficiencies in the IPPC report for SNCR (10 to 85 percent) and SCR (85 to 95 percent) are close to but slightly greater than those reported in the 1994 ACT document (30 to 70 percent and 80 to 90 percent respectively).

Table 4-5.5. NOx Control Techniques Summary From European Best Available Techniques Report[1]

Technique	Kiln Systems Applicability	Reduction Efficiency	Reported Emissions	
			$mg/Nm^{3\,a}$	kg/tonne[b] (lb/ton)
Flame cooling	All	0 to 50%	400	0.8 (1.6)
Low-NOx burner	All	0 to 30%		
Staged combustion	Preheater and Precalciner	10 to 50%	<500 to 1000	< 1.0 to 2.0 (2.0 to 4.0)
Mid-kiln firing	Wet and long dry	20 to 40%	no info	no info
SNCR	Preheater and Precalciner	10 to 85%	200 to 800	0.4 to 1.6 (0.8 to 3.2)
SCR - data from pilot plants only	Possibly all	85 to 95%	100 to 200	0.2 to 0.4 (0.4 to 0.8)

[a] Normally referring to daily averages, dry gas, 273 K, 101.3 kPa and 10% O2.
[b] kg/tonne clinker is based on 2000 m^3/tonne of clinker.

The IPPC report concludes that BAT for reducing NO_x emissions are a combination of general primary measures, primary measures to control NO_x emissions, staged combustion and SNCR. The BAT emission level associated with the use of these techniques is 0.4 to 1.0 lb/ton of clinker (200-500 mg NO_x /m^3 (as NO_2)). This emission level could be seen in context of the current reported emission range of 0.4 to 6.0 lb/ton of clinker (<200-3000 mg NO_x /m^3), and that the majority of kilns in the European Union is said to be able to achieve less than 2.4 lb/ton of clinker (1200 mg/m^3) with primary measures.[1]

While there was support for the above concluded BAT to control NO_x emissions, there was an opposing view that the BAT emission level associated with the use of these techniques is 1.0 to 1.6 lb/ton of clinker (500-800 mg NO_x /m^3 (as NO_2)). There was also a view that selective catalytic reduction is BAT with an associated emission level of 0.2 to 0.4 lb/ton of clinker (100-200 mg NO_x /m^3 (as NO_2)).[1]

5.0 CHEMISTRY OF ELLIS COUNTY MATERIALS AND IMPACTS ON CONTROL DETERMINATIONS

Analysis was conducted to determine the chemical, mineral and elemental composition of limestone and other raw materials used in clinker production in Ellis County. Total organic carbon, total sulfur, various forms of sulfur including sulfite and sulfate, chloride, and total Kjeldahl nitrogen content were determined. Three samples of each type (dry powder, wet slurry, slag) were collected from representative operating kiln sites using Ellis County limestone feed material. Analyses were chosen based on the need to identify composition that was expected to affect NO_x emissions or control option performance.

Total organic carbon results are determined using a technique known as differential scanning calorimetry (DSC). Analyses are carried out in gas with a composition of 20% carbon dioxide, 3% oxygen, and 77% nitrogen similar to the basic constituents of kiln flue gas. This causes an oxidative pyrolysis, which closely parallels actual kiln conditions. The formation of char residues is very unlikely for this testing method. Several samples were also analyzed by an alternative technique that gradually heats the material electrically from an external source using Nitrogen is the carrier gas. The results reflect a pyrolysis regimen and provide additional supplemental data on the temperature profile at which carbon is released.

Total Kjeldahl Nitrogen (TKN) is a measure of organic nitrogen and ammonia in any form found in the samples. Total nitrogen results are determined by a heated digestion of the samples. The ammoniacal nitrogen is the most volatile form of nitrogen. The TKN test does not measure nitrite, and nitrate. Since nitrate and nitrite nitrogen would not react with NO_x they are of little interest for the feed evaluation.

5.1. Results

There are some distinct differences among the feed types that are independent of the incinerator site or treatment. Slag is a manufactured feed material and has lower content of some of the key chemicals of concern for emissions control or new control technology application. For instance, nitrogen and total sulfur in slag is less than the amount found in wet slurry or dry powder, sulfate in slag and slurry less than sulfate in dry powder, and pyritic sulfur in slag is present at lower concentrations than pyritic sulfur in all other feeds types. As a percent of total

mass, organic sulfur tends to be higher in slag than other feed materials. There is a caveat: The methodology used by the laboratory lumps organic sulfur with simple sulfide (non pyrite). The sulfate in feed tends to be relatively constant compared to other compounds tested in the feed material. Site specific results of kiln feed sample chemical analysis are summarized in confidential attachments for each kiln site (Appendix A,B, and C Tables 1 through 5). Results are summarized in the remainder of this section.

5.1.1. Organic Carbon

One set of kiln feed materials had higher organic content than all others. Organic carbon in these dry feed materials is much greater than in all other feed material. Organic carbon in wet slurry from the same site is also higher than the organic carbon in other slurry feed materials. One kiln dry feed material had higher total organic carbon than the others in this sample set. The highest carbon containing feed material also contained higher organic nitrogen. This site also demonstrated lower NOx emissions than other sites. Results for feed sample carbon analysis from this site are provided in confidential data Appendix A.

The lowest organic carbon content was found in dry powder limestone feed from a different site and supplier. The Organic content in these feed materials is quite variable, Total nitrogen was also lower in samples from the same site. This site demonstrates higher NOx emission than other comparable sites. Results of percent carbon analysis in feed are shown in confidential data Appendix B.

Most of the organic material in the dry feed is released between 350 and 500 degrees C indicating high molecular weight organic or pure carbon material. It was noted in the DSC data that some of the samples began generating heat at temperatures below 150°C, while others only began above 200°C. The higher temperatures required to liberate the carbon are a function of the volatility (molecular weight) of the carbonaceous material. It is not known whether this has any effect on NO_x emissions, but could influence VOC emissions. However, NO_x emissions were lower from the site supplying samples containing higher molecular weight carbon Efforts to control VOC emission should take into account the resulting oxidative conditions that do not favor reduction of NO_x.

The pattern of organic combustion determined by DSC appears to be fairly similar for all samples, except of course the slags. Much of the exothermic activity at 400-450°C for all kiln

feeds is probably attributable to pyrite oxidation. In preheater kilns, this may be occurring in Stage 2 of the preheater. Whether this has any impact on NOx emissions is questionable. It is possible, of course, that nascent, freshly formed SO_2 may reduce NO_2.

The results for total heat generated during carbon analysis by the alternative nitrogen purged technique appear to be higher for samples containing higher molecular weight carbon. The heat release results for these higher carbon containing samples show characteristics indicating considerable amounts of char, as evidenced by the lower heating results vis-à-vis the DSC results on samples analyzed using both approaches. If this char is produced in the kiln, it may serve as a reducing agent for NO_x assuming it was available in the hot zone of the process, or it may be oxidized to CO which itself may be acting as a reducing agent.. The additional carbon could be a partial explanation for the very low NO_x emissions at this site.

5.1.2. Total Kjeldahl Nitrogen

The high carbon content feed also has the highest Total Kjeldahl Nitrogen (TKN) content. Dry powder feed from this site contains slightly more Total Kjeldahl nitrogen (TKN) than similar dry feed materials from other sites. While the ratio of %carbon to TKN feed materials is approximately the same for all samples, the total carbon and TKN in wet slurry from sites generating higher NO_x is less than that found in sites using dry powder limestone feed that generate lower NO_x emissions. Results sorted by TKN values are shown in separate tables in confidential Appendices A-4, B-4, and C-4. Assuming the TKN nitrogen is the nonvolatile nitrogen component of the feed, it is likely to be organic based and that nitrogen and carbon are released in the process from the feed at approximately the same time. Such nitrogen release could act as a source of ammoniacal nitrogen at high temperatures, which could establish a quasi-"SNCR/SCR" reductive path for NO, particularly in the presence of iron based catalysts, which at that point in the process has not yet been converted to the ferrite phase of cement clinker, and so may exert a catalytic action. This is admittedly unproven.

5.1.3. Total Sulfur

Total Sulfur and speciated sulfur results are shown in Appendix A, B, and C confidential tables A-4 through C-4. Total Sulfur in samples with higher carbon and nitrogen is generally

higher than total sulfur from other kiln sites. Total sulfite in dry feed material follows the same trend with the highest carbon containing material also showing the highest sulfur as sulfite.. Pyritic Sulfur content in high organic samples trends higher than other kiln sites.

5.2. Conclusions

Total carbon nitrogen and sulfur content seem to be major factors in the difference between kiln feed materials. TKN can impact NO_x emissions by oxidation to NO, but also as a component that may reduce NO formed in the burning zone, by a reaction similar to SNCR or SCR. We do not know the temperature profile of organic nitrogen generation from these feeds, only that nitrate or nitrite nitrogen is not reflected in the values. However, process emissions tests from the site providing highest carbon organic nitrogen and sulfur also show the lowest uncontrolled NO_x release. Other sites use dry powder feed material contains slightly lower levels of TKN but do not show the organic carbon or nitrogen content found in the lower NO_x emitting site.

Feed nitrogen under high carbon loading may be released into a reducing environment and need not generate NO. The temperatures required for organic carbon and nitrogen release are too cold for authentic SNCR, and the process doesn't have the right catalysts for SCR. However, the low NO emissions at the site with the higher carbon in feed limestone suggest that these latter reactions may be occurring. One possible conclusion from the feed analysis information is a reaction under reducing conditions, similar to SNCR or SCR, as follows:

$$CO + NO ==> CO_2 + N$$

$$12NH3 \text{ (from TKN in feed)} + 8NO + 5\ O_2 ==> 10N2 + 18H_2O$$
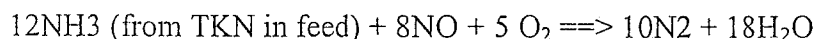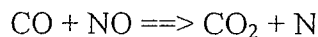
While this site may not have the right temperature/oxygen/CO conditions in the tower for SNCR to be maximally effective, there seems to be some combination of chemistry and process conditions occurring that reduces the NO_x emissions. Further evidence of this possibility can be found in a paper from Zement-Kalk-Gips (German cement journal) written by M. Ono and co-workers, Japan, the authors show the effects of certain iron compounds in catalyzing the reaction of carbon monoxide with NO at temperatures below those usual in SNCR.

It is possible that the calciner design and process conditions at the site with the lowest NOx emissions may be better in general or that its design may produce the right conditions for reduced NOx emissions with the higher carbon/higher organic nitrogen containing feed. Several additional feed analyses (e.g. temperature related nitrogen release, speciated metals analysis) coupled with measurement of gases in kiln emissions are necessary to validate this conclusion.

SO_2 is a high-temperature scavenger for high oxygen radicals like OH· and O·, and may thereby help reduce NO_x. Feed material containing higher carbon and a higher level of sulfur than other kiln feed materials may contribute to the reducing environment and lower NO_x emissions. The "organic sulfur" found in samples also includes sulfide (nonpyritic) sulfur. Sulfite is not usually present in materials taken directly from ore deposits. There is more sulfite in the feed at the lower NO_x emission site than in the other feed from the other sites. This may reflect the return kiln dust and its sulfite content, which in turn may reflect the effect of oxygen upstream of the dust collector. If the available O_2 is lower in the kiln process gas this may also reduce low temperature formation of NO.

6.0   REFERENCES

ATTACHMENT B

ATTACHMENT B

Sample Acquisition and Handling

Clean, clear, pre-labeled, one (1) liter sample bottles were shipped to each Kiln site on August __, 2005 via Federal Express.

on August

All were samples returned to ERG's analytical laboratory with chain of custody and security seals. ERG consulted with three cement kiln experts, F. MacGregor Miller, Gabriel Miller, and David Gossman on the analyses required to determine key features of the kiln feed chemistry important to NOx emissions and control. Recommendations were sought from the experts on laboratories experienced in each analysis. Three laboratories were ultimately selected on the basis of expertise and price. Table 1 summarizes the analyses requested for each sample.

ERG repackaged samples for distribution to the specialty analysis laboratories scheduled to perform feed material composition analysis. Repackaged samples were give unique identification numbers to keep Kiln identity anonymous to the analysis laboratories.

Table 1. Feed Chemical Composition

Plant Name	Samples Received	Sample Type	Total Sulfur	Sulfate	Sulfite	Pyritic Sulfur	Organic Sulfur	Chloride	Nitrogen (TKN)	VOCs
			X	X	X	X	X	X	X	X
			X	X	X	X	X	X	X	X
			X	X	X	X	X	X	X	X
			X	X	X	X	X	X	X	X
			X	X	X	X	X	X	X	X
			X	X	X	X	X	X	X	X
			X	X	X	X	X	X	X	X